Section 6

Quality Assurance/Quality Control

In field sampling with the dilution sampling system, the following quality control procedures were implemented:

- A leak check of the dilution sampling system was performed before field testing was initiated;
- Pitot tubes and meter boxes were calibrated;
- The analytical balance(s) were calibrated;
- Flow control collection devices for the canisters were calibrated using a primary flow standard;
- Multipart forms recording field conditions and observations were used for canisters and carbonyl samples; and
- Strict chain of custody documentation for all field samples was maintained.

Field sampling equipment quality control requirements that were met in the course of preparing for the field test and execution of testing activities are summarized in Table 6-1.

Strict chain of custody procedures were followed in collecting and transporting samples and sampling media to and from the field sampling location. Sample substrates (filters, denuders, PUF canister, DNPH cartridges) were prepared in advance in accordance with the number and types of samples designated in the sampling matrix of the approved field test plan. Clean SUMMA® collection canisters and DNPH cartridges used to collect carbonyl compounds were prepared and supplied by ERG. The PUF, XAD-4®, denuder, and PM-2.5 sampling substrates were prepared and supplied by EPA. Chain of custody forms (Figure 6-1) were

Table 6-1. Field Sampling Equipment Quality Control Measures

Equipment	Effect	Acceptance Criteria	Criteria Achieved?
Orifice meters (volumetric gas flow calibration)	Ensures the accuracy of flow measurements for sample collection	± 1%	Yes
Venturi meters (volumetric gas flow calibration)	Ensures the accuracy of flow measurements for sample collection	± 1% of reading	Yes
Flow transmitter (Heise gauge with differential pressure)	Ensures the accuracy of flow measurements for sample collection	± 0.5% of range	Yes
Analytical Balances	Ensures control of bias for all project weighing	Calibrated with Class S weights	Yes
Thermocouples	Ensures sampler temperature control	±1.5 $^{}$C	Yes
Relative humidity probes	Ensures the accuracy of moisture measurements in the residence chamber	± 2% relative humidity	Yes
Sampling equipment leak check and calibration (before each sampling run)	Ensures accurate measurement of sample volume	1%	Yes
Sampling equipment field blanks	Ensures absence of contamination in sampling system	< 5.0% of sample values	Yes

Reference. EPA Quality Assurance Project Plan - Source Sampling for Fine Particulate Matter (U.S. EPA, 2001).

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Chain of Custody Record

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PROJECT			NO. OF CONTAINERS	ANALYSES						REMARKS	SAM ID NO. *(For lab use only)*
SITE											
COLLECTED BY (*Signature)*											
FIELD SAMPLE I.D.	SAMPLE MATRIX	DATE/TIME									

REMARKS:									RELINQUISHED BY:	DATE	TIME
RECEIVED BY:	DATE	TIME	RELINQUISHED BY:	DATE	TIME	RECEIVED BY:	DATE	TIME	RELINQUISHED BY:	DATE	TIME

LAB USE ONLY

RECEIVED FOR LABORATORY BY:	DATE	TIME	AIRBILL NO.	OPENED BY	DATE	TIME	TEMP°C	SEAL #

Figure 6-1. ERG chain of custody form.

started when the sampling media were prepared; each sample substrate was assigned a unique identification number by the laboratory supplying the substrates.

Sample identification numbers include a code to track:

- Source type;
- Test date;
- Sampler type;
- Substrate type;
- Sampler chamber (i.e., dilution chamber or residence chamber);
- Sampler port;
- Lane/leg;
- Position; and
- Holder number.

For samples to be analyzed in the EPA laboratories, whole sampling arrays were assembled by EPA, assigned a unique tracking number, and used for sample collection. Sample collection arrays were recovered in the field as a complete unit and transferred to the EPA laboratory for disassembly and analysis.

After collection, samples were transported to the analysis laboratories by ERG, with careful documentation of sample collection and chain of custody records for the samples being transported. Samples were stored in a secure area until they were transported to the laboratories performing analyses.

Carbonyl Compound Analysis

Quality control criteria for the carbonyl analysis performed by ERG are shown in Table 6-2. Supporting analytical data are a part of the project file at ERG.

Table 6-2. Carbonyl Analysis: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
HPLC Column Efficiency	Analyze second source QC sample (SSQC)	At setup and 1 per sample batch	Resolution between acetone and propionaldehyde ≥ 1.0 Column efficiency > 500 plates	Eliminate dead volume, backflush, or replace column; repeat analysis	Yes
Linearity Check	Analyze 5-point calibration curve and SSQC in triplicate	At setup or when calibration check does not meet acceptance criteria	Correlation coefficient ≥0.999, relative error for each level against calibration curve ± 20% or less Relative Error	Check integration, re-integrate or re-calibrate	Yes
			Intercept acceptance should be ≥10,000 area counts/compound; correlates to 0.06 mg/mL	Check integration, re-integrate or re-calibrate	Yes
Retention time	Analyze calibration midpoint	Once per 10 samples	Acetaldehyde, Benzaldehyde, Hexaldehyde within retention time window established by determining 3 σ or ± 2% of the mean calibration and midpoint standards, whichever is greater	Check system for plug, regulate column temperature, check gradient and solvents	Yes
Calibration Check	Analyze midpoint standard	Once per 10 samples	85-115% recovery	Check integration, re-calibrate or re-prepare standard, re-analyze samples not bracketed by acceptable standard	Yes

(Continued)

Table 6-2. (Continued)

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved ?
Calibration Accuracy	SSQC	Once after calibration in triplicate	85-115% recovery	Check integration; re-calibrate or re-prepare standard, re-analyze samples not bracketed by acceptable standard	Yes
	Analyze 0.1 µg/mL standard	Once after calibration in triplicate	± 25% difference		
System Blank	Analyze acetonitrile	Bracket sample batch, 1 at beginning and 1 at end	Measured concentration ≤ 5 x MDL	Locate contamination and document levels of contamination in file	Yes
Duplicate Analyses	Duplicate Samples	As collected	± 20% difference	Check integration; check instrument function; re-analyze duplicate samples	Yes
Replicate Analyses	Replicate injections	Duplicate samples only	≤ 10% RPD for concentrations greater than 1.0 µg/mL	Check integration, check instrument function, re-analyze duplicate samples	Yes
Method Spike/Method Spike Duplicate (MS/MSD)	Analyze MS/MSD	One MS/MSD per 20 samples	80-120% recovery for all compounds	Check calibration, check extraction procedures	Yes

Concurrent Air Toxics/Speciated Nonmethane Organic Compound Analysis

The analytical system performing the concurrent analysis is calibrated monthly and blanked daily prior to sample analysis. A quality control standard is analyzed daily prior to sample analysis to ensure the validity of the current monthly response factor. Following the daily quality control standard analysis and prior to the sample analysis, cleaned, dried air from the canister cleaning system is humidified and then analyzed to determine the level of organic compounds present in the analytical system. Upon achieving acceptable system blank results -- less than or equal to 20 ppbC -- sample analysis begins. Ten percent of the total number of samples received are analyzed in replicate to determine the precision of analysis for the program. After the chromatography has been reviewed, the sample canister is returned to the canister cleaning laboratory to be prepared for subsequent sample collection episodes or sent to another laboratory for further analysis. Quality control procedures for the Air Toxics and SNMOC analyses are summarized in Table 6-3.

PM Mass Measurements, Elemental Analysis, Water-Soluble Ion Analysis, and GC/MS Analysis

Quality control criteria for EPA analyses (PM mass, elemental analyses, ion chromatography analysis, and GC/MS analysis) are summarized in Tables 6-4 through 6-7; supporting data are included in the project file in the EPA laboratory.

Table 6-3. Quality Control Procedures for the Concurrent Analysis for Air Toxics and SNMOC

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Air Toxics Analysis				
BFB Instrument Tune Check	Daily prior to calibration check	Evaluation criteria in data system software; consistent with Method TO-15	Retune mass spectrometer; clean ion source and quadrupoles	Yes
Five-point calibration bracketing the expected sample concentration	Following any major change, repair, or maintenance if daily quality control check is not acceptable. Calibration is valid for six weeks if calibration check criteria are met.	RSD of response factors ≤ 30% Relative Retention Times (RRTs) for target peaks ± 0.06 units from mean RRT	Repeat individual sample analysis; repeat linearity check; prepare new calibration standards and repeat analysis	Yes
Calibration check using mid-point of calibration range	Daily	Response factor ≤ 30% bias from calibration curve average response factor	Repeat calibration check; repeat calibration curve	Yes
System Blank	Daily following tune check and calibration check	0.2 ppbv/analyte or MDL, whichever is greater Internal Standard (IS) area response ± 40% and retention time ± 0.33 min of most recent calibration check	Repeat analysis with new blank; check system for leaks, contamination; re-analyze blank.	Yes
Laboratory Control Standard (LCS)	Daily	Recovery limits 70% - 130% IS Retention Time ± 0.33 min of most recent calibration	Repeat analysis; repeat calibration curve.	Yes
Replicate Analysis	All duplicate field samples	<30% RPD for compounds >5xMDL	Repeat sample analysis	Yes
Samples	All samples	IS RT ± 0.33 min of most recent calibration	Repeat analysis	Yes

(Continued)

Table 6-3. (Continued)

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
SNMOC Analysis				
System Blank Analysis	Daily, following calibration check	20 ppbC total	Repeat analysis; check system for leaks; clean system with wet air	Yes
Multiple point calibration (minimum 5); propane bracketing the expected sample concentration range	Prior to analysis and monthly	Correlation coefficient (r^2) ≥0.995	Repeat individual sample analysis; repeat linearity check; prepare new calibration standards and repeat	Yes
Calibration check: midpoint of calibration curve spanning the carbon range (C_2-C_{10})	Daily	Response for selected hydrocarbons spanning the carbon range within ± 30% difference of calibration curve slope	Repeat calibration check; repeat calibration curve.	Yes
Replicate analysis	All duplicate field samples	Total NMOC within ± 30% RSD	Repeat sample analysis	Yes

Table 6-4. PM Mass Measurements: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Acheived?
Deposition on Filter during Conditioning	Analyze Laboratory Filter Blank	Bracket sample batch, 1 at beginning and 1 at end	Mass within ± 15mg of previous weight	Adjust mass for deposition	Yes
Laboratory Stability	Analyze Laboratory Control Filter	Bracket sample batch, 1 at beginning and 1 at end	Mass within ± 15mg of previous weight	Adjust mass to account for laboratory difference	Yes
Balance Stability	Analyze Standard Weights	Bracket sample batch, 1 at beginning and 1 at end	Mass within ± 3mg of previous weight	Perform internal calibration of balance, perform external calibration of balance	Yes

Table 6-5. Elemental Analysis: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Performance Evaluation check	Analyze Monitor Sample	Once per month	≤ 2% change in each element from previous measurement	Recalibrate	Yes

Table 6-6. Water-Soluble Ion Analysis: Quality Control Criteria

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Linearity Check	Analyze 4-point calibration curve	At setup or when calibration check does not meet acceptance criteria	Correlation coefficient ≥0.999	Recalibrate	Yes
System Dead Volume	Analyze water	Bracket sample batch, 1 at beginning and 1 at end	Within 5% of previous analysis	Check system temperature, eluent, and columns	Yes
Retention Time	Analyze standard	At setup	Each ion within ± 5% of standard retention time	Check system temperature and eluent	Yes
Calibration check	Analyze one standard	Once every 4-10 samples	85-115% recovery	Recalibrate or re-prepare standard, re-analyze sample not bracketed by acceptable standard	Yes
System Blank	Analyze HPLC grade water	Bracket sample batch, 1 at beginning and 1 at end	No quantifiable ions	Re-analyze	Yes
Replicate Analyses	Replicate Injections	Each sample	≤ 10% RPD for concentrations greater than 1.0mg/L	Check instrument function, re-analyze samples	Yes

Table 6-7. Quality Control Procedures for Gas Chromatography-Mass Spectrometry Analysis of Semivolatile Organic Compounds.

Quality Control Check	Frequency	Acceptance Criteria	Corrective Action	Criteria Achieved?
Mass spectrometer instrument tune check	Daily prior to calibration check	Mass assignments m/z = 69, 219, 502 (± 0.2) Peak widths = 0.59-0.65 Relative mass abundances = 100 % (69); ≥30 % (219); ≥ 1% (502).	Retune mass spectrometer; clean ion source	Yes
Five-point calibration bracketing the expected concentration range	Following maintenance or repair of either gas chromatograph or mass spectrometer or when daily quality control check is not acceptable	Correlation coefficient of either quadratic or linear regression ≥ 0.999	Check integration, re-integrate or recalibrate	Yes
Calibration check using midpoint of calibration range	Daily	Compounds in a representative organic compound suite > 80% are ± 15% of individually certified values. Values ≥ 20% are not accepted.	Repeat analysis, repeat calibration curve	Yes
System Blank	As needed after system maintenance or repair	Potential analytes ≤ detection limit values	Repeat analysis; check system integrity. Reanalyze blank	Yes
Retention time check	Daily	Verify that select compounds are within ± 2% of established retention time window	Check inlet and column flows and the various GC/MS temperature zones	Yes